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Note

Study of photopolymerization of methyl methacrylate using morpholine combined with benzophenone as photoinitiator

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Photopolymerization of methyl methacrylate (MMA) has been studied dilatometrically at 40 ± 0.5 °C using morpholine combined with benzophenone (BP) as photoinitiator under irradiation with Hg-vapur lamp (λ = 3600 Å). Initiation of polymerization takes place through the generation of free radicals of morpholine and benzophenone. The inhibition periods are very low ((7 - 21 min) at different concentrations of photoinitiators. Rates of polymerization (R_p) have been determined. The values of initiator exponent (IE) have been calculated for two different systems: (i) morpholine (0.25×10^{-1} mol dm^{-3} to 5×10^{-1} mol dm^{-3}) combined with the fixed concentration of BP (10^{-2} mol dm^{-3}) and (ii) morpholine and BP at equimolar concentrations (1×10^{-1} mol dm^{-3} to 9×10^{-1} mol dm^{-3}). The initiator exponent values have been found to be 0.3 and 0.5, respectively. The kinetics, mechanism and chain termination of the photopolymer reaction have been discussed.

It has been widely reported that organic compoudns containing O,N,S act as photoinitiator[1] in the polymerization of MMA and their mechanisms are known. Compounds containing a heteroatom in a cyclic compoound like pyridine and quinoline also act as photoinitiator[2]. Aliphatic amines and polyamines[3] are used as initiator.. Benzophenone[4] and few aromatic ketones are used as photosensitizer in the polymerization of MMA.

Morpholine, being chemically active, has been used for oxidative polymerization of dimethyl phenol[5], and polymerization of xylenol[6]. Reaction of morpholine with acrylamide or acrylanilide and the kinetics of this reaction have been established[7]. Reactions of morpholine with formaldehyde and hydroxybenzophenones have also been studied.[8]

In the present study the heterocyclic compound morpholine combined with benzophenone has been used as photoinitiator in the polymerization of methyl methacrylate (MMA) under irradiation with Hg - vapour lamp (3600 Å). The kinetics, initiator exponent values (IE) and the mechanism of the photoreactions have been studied.

Methods: A diletometric apparatus was used to study the polymerization reaction according to the procedure described elsewhere.[9] The reactions were carried out under nitrogen atmosphre at 40 ± 0.5 °C in the presence of Hg-vapour lamp (125W, 250 V, Philips, India) as the light source. The polymer formed was isolated by precipitation with petroleum ether in each case. The colour of PMMA was milky white in every experiment.

The graphs of % conversion of polymer formed versus reaction period in min are plotted in **Figures 1** and **3**. From the slopes of these linear curves R_p values were calculated **Figure 1** (I-VI) shows the plots of kinetics when [morpholine] was varied and [BP] kept constant at 10^{-2} mol dm^{-3}. **Figure 3** (I-VI) shows the plots of kinetics at equimolar concentration of morpholine and BP.

Materials: Stabilised methyl methacrylate, collected from Dental products of India Ltd, Bombay, was purified by the usual procedure and redistilled before use. Benzophenone (NOCIL, India) was of reagent grade and recrystallised before performing experiment. Morpholine was obtained form Sarabhai Chemicals,

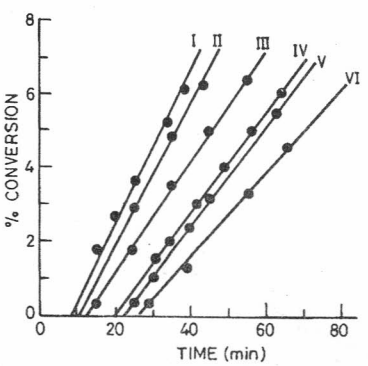


Figure 1—Photopolymerization of MMA in bulk at 40 °C using morpholine - BP system. Concentrations of morpholine are I = 5×10^{-1}, II = 3.75×10^{-1}, III = 2.5×10^{-1}, IV = 1×10^{-1}, V = 0.5×10^{-1}, and VI = 0.25×10^{-1} (in mol dm^{-3}), and concentration of BP is 10^{-2} mol dm^{-3} (fixed).

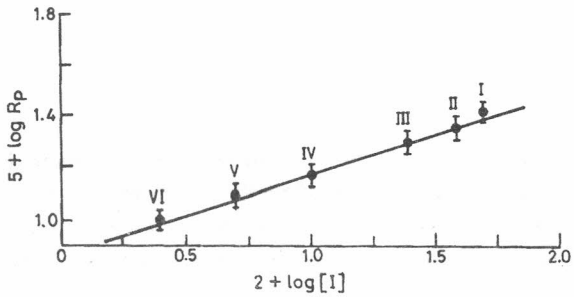


Figure 2—Determination of initiator exponent (IE) value of the first system (vide Figure 1). Plot of log R_p vs. long [I].

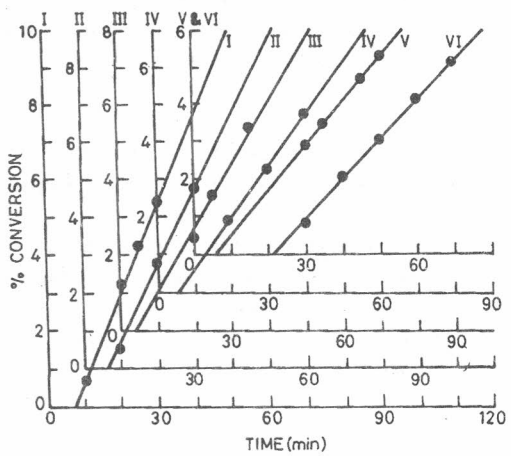


Figure 3—Photopolymerization of Mma in bulk at 40 °C using morpholine - BP (equimolar) system. Concentration of morpholine and BP are: I = 9×10^{-1}, II = 6.7×10^{-1}, III = 4.75×10^{-1}, IV = 2.5×10^{-1}, V = 2×10^{-1}, and VI = 1×10^{-1} (in mol dm^{-3}).

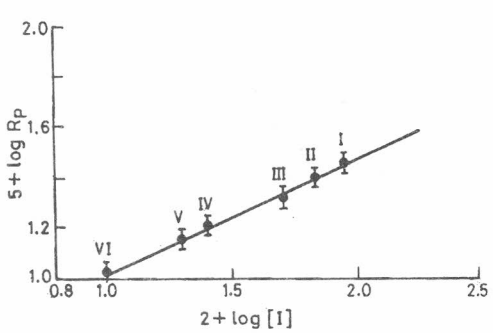


Figure 4—Determination of initiator exponent (IE) value of the second system (vide Figure 3). Plot of long R_p vs. log [I].

Baroda, India and distilled carefully before use. A Hg-vapour lamp (125W, 250V, Philips, India) was used as the source of light.

Results and Discussion

The literature reports that compounds containing O, N, S, etc. may act as photoinitiators. Sometimes inhibition period is high to form photopolymer, and hence the rate of polymerization (R_p) becomes low.

In the present study morpholine was chosen as the photoinitiator which contains one N and one O atom in the molecule.

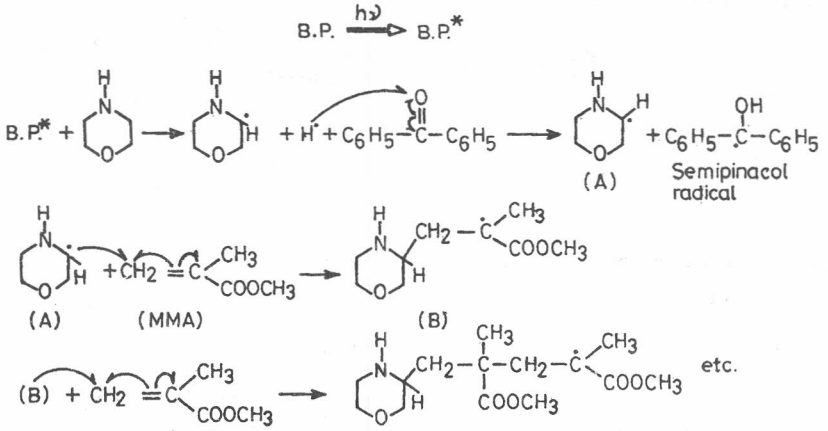
Kinetics of the photopolymerization of MMA using morpholine and BP were carried out extensively in two different systems. At first the concentration of morpholine was varied from 0.25×10^{-1} mol dm^{-3} to 5×10^{-1} mol dm^{-3} and [BP] was fixed at 10^{-2} mol dm^{-3}; the plots are shown in **Figure 1** (I-VI). In the other system morpholine and BP were taken in equimolar concentrations ((1×10^{-1} mol dm^{-3} to 9×10^{-1} mol dm^{-3}) and the plots are shown in **Figure 3** (I-VI).

From **Figures 1** and **3**, R_p values were obtained[1,10] in mol dm^{-3} s^{-1}. The corresponding log R_p and long [I] are plotted in **Figures 2** and **4** (I-VI), respectively where R_p is the rate of polymerization and [I] is the concentration of initiator. From the slopes of the two linear curves (**Figures 2** and **4**), the values of initiator exponent (IE) were found to be 0.3 and 0.5 in the two systems respectively.

The inhibition period was found to be only 7 min to form the polymer when morpholine and BP were taken at the concentration (9×10^{-1} mol dm^{-3} each, (see **Figure 3**). The highest inhibition period was 21 min at 1×10^{-1} mol dm^{-3} concentration. The rate of polymerization R_p decreased depending upon the concentration of morpholine and BP (see **Figure 3**). It was also observed that morpholine or BP could not yeild any polymer when they were used as an initiator seperately under identical irradiation or in the dark. Moreover, their combination also failed to yeild any polymer in the dark even after 24 hr.

The difference between the initiator exponent (IE) values (0.3 and 0.5) is due to the variation of concentrations of morpholine in two different systems (see **Figures 1** and **3**). Moreover, the concentration of BP was lower in the first system than in the second one. This is also a factor responsible for variation of IE values, because lower concentration of BP generates lower triplet concentration level which would lower the rate of polymerization (R_p).

Another reason for a higher value (0.5) of IE in the second system is due to the lower amount of side

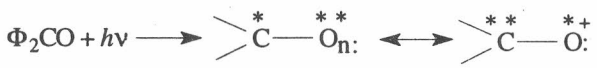


Scheme I

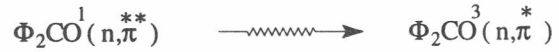
reactions and lower amount of terminations. The chain termination reactions[11] are shown in **Schemes II** and **III**.

The morpholine - benzophenone system was found to be exclusively ineffective for polymerization of MMA in the dark at room temperature.

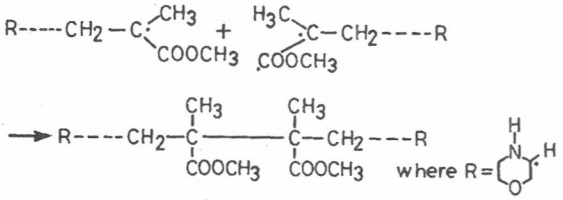
Effect of benzophenone on irradiation. BP was used as photosensitizer in these experiments which become excited in the light (hν) to give benzophenone of triplet state ϕ_2CO^3 (n,π^*). The triplet state transfers energy to the morpholine to build up excited morpholine radicals as shown in **Scheme I**. The excited morpholine radicals initiate the photochemical reaction to form **B** (**Scheme I**). The different states of BP are shown below;



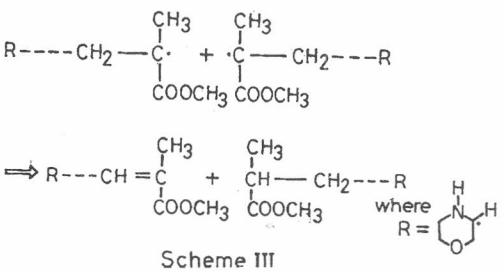
Inter system crossing



Mechamism. The photochemical reaction takes place through the generation of free radical mechanism on irradiation (λ = 3600 Å). Initially BP collects energy from the light source to form triplet of BP ($C_6H_5CO^{\bullet}C_6H_5$). The latter interacts with morpholine and abstracts $H^{\bullet}$ atom from ∝-C-H of the morpholine[12] and BP gets converted to a semipinacol radical[11,13] ($C_6H_5C^*OH\ C_6H_5$) leaving a morpholine radical (**A**) (**Scheme I**). It was observed that two semipinacol radicals combined to form benzopinacol, $(C_6H_5)_2$ COH: COH $(C_6H_5)_2$, on irradiation[14]. The $H^{\bullet}$ radicals were formed from morpholine as given in literature[15].



Scheme II



Scheme III

The morpholine radical **A**, thus formed, initiates polymer reaction in MMA (monomer) to make the radical **B** (**Scheme I**) by radical addition which is chemically stable due to the presence of adjacent >C = O carbonyl group. The polymer chain increased by the addition of other molecules of the monomer. All steps of the mechanism are shown in **Scheme I** which are supported by the literature[11-15].

Termination of polymer chain[16]. Terminations occur by two routes. (i) Termination by combination —

It occurs when two polymer chains combine to form a dead polymer as shown in **Scheme II**. (ii) Termination by disproportionation. It also occurs in these photochemical reactions as shown in **Scheme III**. General termination equation may be represented as

$$\dot{M} + \dot{M} \xrightarrow{K_t} \text{dead polymer product}$$

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